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(54) **Oxygen absorbing resin composition and multi-layer container using the same**

(57) A resin composition obtained by blending a thermoplastic resin that can be melt-extruded at a solubility parameter of not smaller than 9.5 with an organic oxidizing component and with a transition metal catalyst, the organic oxidizing component being a polyene having a functional group on a side chain or at a terminal

thereof. The resin composition has excellent moldability and gas shut-off property. A multi-layer container having an oxygen-absorbing layer of this resin composition exhibits excellent gas-barrier property and is capable of favorably preserving the content.

[0013] A further object of the present invention is to provide a multi-layer container made of the above resin composition, exhibiting excellent oxygen-absorbing property and excellent oxygen-barrier property, and withstanding hot filling and preservation over extended periods of time.

[0014] According to the present invention, there is provided a resin composition obtained by blending a thermoplastic resin that can be melt-extruded at a solubility parameter of not smaller than 9.5 with an organic oxidizing component and with a transition metal catalyst, the organic oxidizing component being a polyene having a functional group on a side chain or at a terminal thereof.

[0015] In the resin composition of the present invention, it is desired that the thermoplastic resin is a gas-barrier resin having an oxygen permeation coefficient of not larger than 7 cc-mm/m²·day-atm (20°C, 0%RH), and is, particularly, a polyamide resin or an ethylene-vinyl alcohol copolymer. Among them, it is desired that the thermoplastic resin is a xylylene group-containing polyamide resin having a concentration of amino end groups of not smaller than 40 eq/10⁶ g.

[0016] It is further desired that the above-mentioned organic oxidizing component is a polybutadiene or a polyisoprene modified with a maleic acid or with an anhydride thereof and that the organic oxidizing component is dispersed in the thermoplastic resin, and the dispersant thereof has a minimum length of not larger than 400 nm.

[0017] Further, it is desired that the above-mentioned transition metal catalyst is an organic salt of cobalt and is contained at a concentration of not smaller than 300 ppm calculated as a metal.

[0018] According to the present invention, further, there is provided a multi-layer container having at least one oxygen-absorbing layer of the above-mentioned resin composition.

[0019] In the multi-layer container, it is desired that a layer of a polyolefin resin or of a thermoplastic polyester resin is formed on at least one side of the oxygen-absorbing layer, the thermoplastic polyester resin having a crystallinity of from 30 to 55% and a half-value width of an X-ray diffraction profile of not larger than 15°.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] Fig. 1 is a graph illustrating how to find a peak A of a diffraction profile and a half-value width B from the intensity profile of the diffraction profile relying upon the X-ray analysis.

DETAILED DESCRIPTION OF THE INVENTION

[0021] The resin composition of the present invention contains a thermoplastic resin, an organic oxidizing component and a transition metal catalyst, and has a feature in the combination of the thermoplastic resin which is the one having a solubility parameter (Sp-value) of not smaller than 9.5 and is capable of being melt-extruded, and the organic component capable of being oxidized (also referred to as organic oxidizing component) which is a polyene having a functional group on a side chain or at a terminal thereof.

[0022] It is important that the thermoplastic resin used in the present invention has a solubility parameter of not smaller than 9.5 from the standpoint of gas shut-off property and strength of the resin composition.

[0023] In this specification, the solubility parameter (Sp-value) is defined to be the coagulation energy density (cal/cc) raised to the power of 1/2, and is intimately related to the strength of the hydrogen bond. The larger the Sp-value is, the greater the strength of the hydrogen bond is.

[0024] The thermoplastic resin used in the present invention plays the role of a principal component of the resin composition i.e., plays the role of a matrix. The thermoplastic resin that has the solubility parameter (Sp-value) lying within the above-mentioned range, exhibits a large hydrogen bond and, hence, excellent gas shut-off property.

[0025] Further, the thermoplastic resin having the solubility parameter (Sp-value) lying within the above-mentioned range, has a large coagulation energy density, enables the resin composition to exhibit a large mechanical strength, and imparts a satisfactory moldability.

[0026] In the present invention, a polyene having a functional group on a side chain or at a terminal thereof is used as an organic oxidizing component. The organic oxidizing component is oxidized solely by the action of a transition metal catalyst that will be described later to absorb oxygen. As the organic oxidizing component, there is used the one having a functional group on a side chain or at a terminal thereof so as to be favorably dispersed in the thermoplastic resin to thereby obtain excellent workability and to promote the absorption of oxygen by the oxidation of the organic oxidizing component.

[0027] In the organic oxidizing component, it is considered that hydrogen atoms are easily pulled out at positions of active carbon atoms of the organic component thereby to generate a radical. The composition containing the transition metal catalyst and the above organic oxidizing component absorbs oxygen through the oxidation of the organic component, as a matter of course. Here, it is believed that the oxidation takes place through the elementary processes of ① generation of radicals due to the pull-out of hydrogen atoms from the carbon atoms neighboring the double bond by the transition metal catalyst, ② generation of peroxy radicals due to the addition of oxygen molecules to the radicals, and ③ pull-out of hydrogen atoms by peroxy radicals.

it is desired to use homopolymers such as polymetaxylyleneadipamide, polymetaxylylenesbacamide, polymetaxylylenesubaramide, polyparaxylylenepimeramide and polymetaxylyleneazeraamide; copolymers such as metaxylylene/paraxylyleneadipamide copolymer, metaxylylene/paraxylylenepimeramide copolymer, metaxylylene/paraxylylenesbacamide copolymer and metaxylylene/paraxylyleneazeraamide copolymer; and copolymers of these homopolymers or copolymers with an aliphatic diamine such as hexamethylenediamine, an alicyclic diamine such as piperadine, an aromatic diamine such as para-bis(2-aminoethyl)benzene, an aromatic dicarboxylic acid such as terephthalic acid, a lactam such as ω -caprolactam, an ω -aminocarboxylic acid such as 7-aminoheptanoic acid, or an aromatic aminocarboxylic acid such as para-aminomethylbenzoic acid. Among them, there can be particularly preferably used a diamine component comprising chiefly an m-xylylenediamine and/or a p-xylylenediamine, and a polyamide obtained from an aliphatic dicarboxylic acid and/or an aromatic dicarboxylic acid.

[0045] These xylylene group-containing polyamides exhibit superior oxygen-barrier property to those of other polyamide resin, and are desired for accomplishing the object of the present invention.

[0046] In the present invention, it is desired that the polyamide resin has a amino end group concentration of not smaller than $40 \text{ eq}/10^6 \text{ g}$ and, more preferably, not smaller than $50 \text{ eq}/10^6 \text{ g}$ from the standpoint of suppressing the polyamide resin from being deteriorated by oxidation.

[0047] There is a close relationship between the deterioration of the polyamide resin by oxidation, i.e., absorption of oxygen and the concentration of amino end groups of the polyamide resin. That is, when the concentration of the amino end groups of the polyamide resin is in the above-mentioned relatively high range, the rate of absorbing oxygen is suppressed to be almost zero or to be close to zero. When the concentration of the amino end groups of the polyamide resin becomes smaller than the above-mentioned range, on the other hand, the polyamide resin tends to exhibit an increased rate of absorbing oxygen.

[0048] It is desired that these polyamides, too, have molecular weights large enough for forming a film, and have relative viscosities (η_{rel}) of not smaller than 1.1 and, particularly, not smaller than 1.5 as measured in a concentrated sulfuric acid of a concentration of 1.0 g/dl at a temperature of 30°C .

[0049] As the thermoplastic resin, there can be used a thermoplastic polyester such as a polyethylene terephthalate derived from an aromatic dicarboxylic acid such as terephthalic acid or isophthalic acid and from diols such as ethylene glycol.

[0050] It is also possible to use a so-called gas-barrier polyester having excellent gas-barrier property.

[0051] The gas-barrier polyester contains, in a polymer chain, a terephthalic acid component (T) and an isophthalic acid component (I) at a molar ratio of T:I = 95:5 to 5:95 and, particularly, 75:25 to 25:75, and contains an ethylene glycol component (E) and a bis(2-hydroxyethoxy)benzene component (BHEB) at a molar ratio of E:BHEB = 99.999:0.001 to 2.0:98.0 and, particularly, 99.95:0.05 to 40:60. As the BHEB, there can be preferably used a 1,3-bis(2-hydroxy)benzene.

[0052] It is desired that the polyester (BPR), usually, has a molecular weight at least large enough forming a film and has an intrinsic viscosity $[\eta]$ of from 0.3 to 2.8 dl/g and, particularly, from 0.4 to 1.8 dl/g as measured in a mixture solvent of phenol and tetrachloroethane at a weight ratio of 60:40 at a temperature of 30°C .

[0053] It is desired that the thermoplastic resin used for the resin composition of the present invention has gas-barrier property as described above and has an oxygen permeation coefficient which is not larger than $7 \text{ cc}\cdot\text{mm}/\text{m}^2\cdot\text{day}\cdot\text{atom}$ (20°C , 0%RH).

[Organic Oxidizing Component]

[0054] The organic oxidizing component used in the present invention has a functional group on a side chain or at a terminal thereof and is capable of being oxidized.

[0055] The organic component capable of being oxidized desirably has active carbon atoms enabling hydrogen to be easily pulled out. Though there is no particular limitation, such active carbon atoms may be those carbon atoms neighboring the carbon-carbon double bond, tertiary carbon atoms to which a carbon side chain is bonded or active methylene groups.

[0056] As the functional group existing on a side chain or at a terminal, there can be exemplified carboxylic acid group, carboxylic anhydride group, group of carboxylate, group of carboxylic acid ester, group of carboxylic acid amide, carbonyl group and hydroxyl group.

[0057] As the organic oxidizing component, there can be used a polyene oligomer or a polymer modified with an acid or an acid anhydride.

[0058] As the polyene, there can be preferably used a polyene having 4 to 20 carbon atoms or a resin containing a unit derived from a chain-like or cyclic conjugated or non-conjugated polyene.

[0059] As these monomers, there can be exemplified conjugated dienes such as butadiene and isoprene; chain-like non-conjugated dienes such as 1,4-hexadiene, 3-methyl-1,4-hexadiene, 4-methyl-1,4-hexadiene, 5-methyl-1,4-hexadiene, 4,5-dimethyl-1,4-hexadiene and 7-methyl-1,6-octadiene; cyclic non-conjugated dienes such as methyltetrahy-

[0075] As the complex of the transition metal, on the other hand, there can be used a complex with a β -diketone or a β -keto-acid ester. As the β -diketone or the β -keto-acid ester, there can be used, for example, acetylacetone, acetoethyl succinate, 1,3-cyclohexadion, methylene bis-1,3-cyclohexadion, 2-benzyl-1,3-cyclohexadione, acetyl tetralone, palmitoyl tetralone, stearoyl tetralone, benzoyl tetralone, 2-acetylcyclohexanone, 2-benzoylcyclohexanone, 2-acetyl-1,3-cyclohexanedion, benzoyl-p-chlorobenzoylmethane, bis(4-methylbenzoyl)methane, bis(2-hydroxybenzoyl)methane, benzoylacetone, tribenzoylmethane, diacetylbenzoylmethane, stearoylbenzoylmethane, palmitoylbenzoylmethane, lauroylbenzoylmethane, dibenzoylmethane, bis(4-chlorobenzoyl)methane, bis(methylene-3,4-dioxybenzoyl)methane, benzoylacetylphenylmethane, stearoyl(4-methoxybenzoyl)methane, butanoylacetone, distearoylmethane, acetylacetone, stearoylacetone, bis(cyclohexanoyl)-methane and dipivaloylmethane.

[Resin Composition]

[0076] It is desired that the resin composition of the present invention contains the organic oxidizing component in an amount of from 0.01 to 10% by weight and, particularly, from 1.0 to 7% by weight.

[0077] It is further desired that the resin composition contains a transition metal catalyst in an amount of at least 300 ppm and, particularly, from 310 to 800 ppm calculated as a transition metal.

[0078] When the amount of the organic oxidizing component is smaller than the above-mentioned range, the oxygen-absorbing property tends to be deteriorated as compared with when the amount of the organic oxidizing component lies within the above-mentioned range. When the amount of the organic oxidizing component becomes more than the above-mentioned range, on the other hand, no distinguished advantage is obtained concerning the oxygen-absorbing property, and the resin composition exhibits decreased strength, deteriorated gas shut-off property and poor moldability, which is not desirable.

[0079] When the amount of the transition metal catalyst becomes smaller than the above-mentioned range, the oxygen-absorbing property tends to be deteriorated as compared with when the amount of the transition metal catalyst lies within the above-mentioned range. When the amount of the transition metal catalyst exceeds the above-mentioned range, on the other hand, the resin composition tends to be deteriorated, which is not desirable, either.

[0080] The thermoplastic resin can be blended with the organic oxidizing component and with the transition metal catalyst by a variety of means. They can be blended in any order without limitation.

[0081] For example, the thermoplastic resin is dry-blended or melt-blended with the organic oxidizing component so as to easily prepare a blend of the two. The transition metal catalyst, on the other hand, is used in a small amount compared to the thermoplastic resin or the organic oxidizing component. In order to accomplish the homogeneous blending, therefore, the transition metal catalyst is usually dissolved in an organic solvent, and the solvent and the powdery or granular thermoplastic resin as well as the oxidizing polymer are mixed together, and, as required, the mixture is dried in an inert atmosphere.

[0082] As the solvent for dissolving the transition metal catalyst, there can be used an alcohol solvent such as methanol, ethanol or butanol; an ether solvent such as dimethyl ether, diethyl ether, methyl ethyl ether, tetrahydrofuran or dioxane; a ketone solvent such as methyl ethyl ketone or cyclohexanone; or a hydrocarbon solvent such as n-hexane or cyclohexane. In general, the transition metal catalyst is dissolved at a concentration of from 5 to 90% by weight.

[0083] It is desired that the mixing of the thermoplastic resin, organic oxidizing component and transition metal catalyst and the subsequent preservation thereof, are conducted in a non-oxidizing atmosphere such that the composition is not oxidized in the preceding stage. For this purpose, it is desired to mix and dry them under a reduced pressure or in a nitrogen stream.

[0084] The mixing and drying can be executed by using an extruder or an injection machine which is of the ventilation type or is equipped with a dryer in a step preceding the molding step.

[0085] It is further allowable to prepare a master batch of a thermoplastic resin and/or an oxidizing polymer containing the transition metal catalyst at a relatively high concentration, and dry-blend the master batch with a non-blended thermoplastic resin, thereby to prepare an oxygen-absorbing resin composition of the present invention.

[0086] According to the present invention, the polyamide resin is used as the thermoplastic resin after being dried under generally employed drying conditions of a temperature of from 120 to 180°C under a pressure of from 0.5 to 2 mmHg for 2 to 6 hours.

[0087] Though generally not required, the resin composition of the present invention may, as desired, be blended with a known activating agent. Preferred examples of the activating agent include polyethylene glycol, polypropylene glycol, ethylene-vinyl alcohol copolymer, ethylene-methacrylic acid copolymer, and hydroxyl group- and/or carboxyl group-containing polymers such as various ionomers.

[0088] These hydroxyl group- and/or carboxyl group-containing polymers can be blended in an amount of not larger than 30 parts by weight and, particularly, in an amount of from 0.01 to 10 parts by weight per 100 parts by weight of the thermoplastic resin.

[0089] The resin composition of the present invention may be blended with filler, coloring agent, heat-resistant sta-

COC/PET

Seven-layer structure: PET/OAR/COC/PET/EVOH/OAR/PET

[0103] In preparing the laminated-layer structure, an adhesive resin may, as required, be interposed among the resin layers.

[0104] As the above-mentioned adhesive resin, there can be exemplified a thermoplastic resin containing a carbonyl (-CO-) group based on carboxylic acid, carboxylic anhydride, carboxylate, carboxylic acid amide or carboxylic acid ester on the main chain or on the side chain at a concentration of 1 to 700 milliequivalents (meq)/100 g of the resin and, particularly, at a concentration of 10 to 500 meq/100 g of the resin. Preferred examples of the adhesive resin include ethylene-acrylic acid copolymer, ionically crosslinked olefin copolymer, maleic anhydride-grafted polyethylene, maleic anhydride-grafted polypropylene, acrylic acid-grafted polyolefin, ethylene-vinyl acetate copolymer, copolymerized polyester and copolymerized thermoplastic resin, which may be used in one kind or in a combination of two or more kinds. These resins are useful for laminating the layers by the simultaneous extrusion or by the sandwich lamination.

[0105] The pre-formed gas-barrier resin film and the humidity-resistant resin film are adhered and laminated by also using a thermosetting adhesive resin such as isocyanate or epoxy.

[0106] In the multi-layer container having the oxygen-absorbing layer comprising resin composition of the present invention, there is no particular limitation on the thickness of the oxygen-absorbing layer. Generally, however, it is desired that the thickness of the oxygen-absorbing layer is in a range of from 1 to 100 μm and, particularly, from 5 to 50 μm . Namely, when the thickness of the oxygen absorbing layer becomes smaller than a given range, the oxygen-absorbing performance is deteriorated. Even when the thickness of the oxygen absorbing layer becomes larger than the given range, on the other hand, no distinguished advantage is obtained concerning the oxygen-absorbing performance but the amount of the resin increases bringing about disadvantage in economy and container properties such as drop in the flexibility and softness of the materials.

[0107] The total thickness of the multi-layer packaging material of the present invention may differ depending upon the use but is, usually, from 30 to 7000 μm and, particularly, from 50 to 5000 μm . It is, on the other hand, desired that the thickness of the oxygen-absorbing intermediate layer is from 0.5 to 95% and, particularly, from 1 to 50% of the whole thickness.

[0108] The multi-layer container of the present invention can be produced by a known method except the use of the oxygen-absorbing layer of the above-mentioned resin composition.

[0109] For example, the film, sheet or tube is formed by melt-kneading the above-mentioned resin composition by using the extruder and, then, extruding it into a desired shape through a T-die or a circular die (ring die). Namely, a T-die method film and a blown film are obtained. The T-die film is biaxially stretched to obtain a biaxially stretched film.

[0110] The resin composition is melt-kneaded by using the injection machine and is, then, injected into an injection metal mold to obtain a container and a preform for producing the container.

[0111] Further, the resin composition is extruded into a predetermined molten resin mass through the extruder and is compression-molded in a metal mold to obtain the container or the preform for producing the container.

[0112] The molded article may assume the shape of a film, a sheet, a parison or a pipe for forming bottles and tubes, and a preform for producing bottles and tubes.

[0113] The bottle is easily formed from the parison, pipe or preform by pinching off the extruded article by using a pair of split molds and by blowing a fluid therein.

[0114] The pipe or the preform that is cooled is, then, heated at a stretching temperature, stretched in the axial direction through one step or many steps, and is blow-stretched in the circumferential direction with the fluid pressure to obtain a stretch-blown bottle.

[0115] Further, the film or the sheet is subjected to vacuum-molding, pressurized air-molding, stretch-molding or plug-assisted molding to obtain packaging containers of the shape of cups and trays as well as a closure member of a film or a sheet.

[0116] The packaging materials such as films can be used as packaging bags of a variety of forms and can be produced by a known bag-producing method. Examples include ordinary pouches which are sealed along the three sides or the four sides, pouches with a cassette, standing pouches and pillow packaging bags, to which only, however, the invention is in no way limited.

[0117] The multi-layer extrusion-molded article can be produced relying upon a known co-extrusion molding method, i.e., by conducting the extrusion-molding in the same manner as described above but using extruders in a number corresponding to the kinds of the resins and using multi-layer multiple dies.

[0118] Further, the multi-layer injection-molded article can be produced relying upon the co-injection method or the sequential injection method by using injection molding machines in a number corresponding to the kinds of the resins.

[0119] The multi-layer film and the multi-layer sheet can be produced relying upon the extrusion coating method or the sandwich lamination. The multi-layer film or the sheet can also be produced by dry-laminating the films that have

gas: argon), and the amount of oxygen that has permeated through was calculated from the concentration of oxygen.

② A multi-layer container was filled with 3 cc of water and was heat-sealed with an aluminum-containing closure member in a nitrogen atmosphere. The multi-layer container was not treated or was boiled at 85°C for 30 minutes, and was preserved at 30°C-80%RH. The concentration of oxygen in the multi-layer container was measured by using the above gas chromatography, and the amount of oxygen that has permeated through was calculated from the concentration of oxygen.

(2) Measurement of the concentration of oxygen dissolved in the multi-layer container

[0131] The bottle was filled with ultra-pure water heated at 93°C leaving a head space of 15 ml, sealed with a cap, and was immersed in a hot water bath maintained at 77°C for 5 minutes. The multi-layer bottle filled with ultra-pure water was taken out from the hot water bath, and was allowed to naturally cool all night at normal temperature and under normal pressure. Then, the ultra-pure water in the bottle was drained. Thereafter, the multi-layer bottle was filled with oxygen-free water while blowing a nitrogen gas therein, and was sealed with an aluminum cap without permitting air bubbles to enter therein. The multi-layer bottle was preserved at 55°C, and the concentration of oxygen dissolved in the water in the multi-layer bottle was measured by using an instrument for measuring the concentration of oxygen dissolved in water (oxygen indicator: Orbisphere Laboratories).

(3) Measurement of the amount of oxygen absorbed.

[0132] An oxygen-absorbing film was cut into a size of 35 cm², introduced into the HIRETOFLEX (HR78-84W, manufactured by Toyo Seikan Co.) container having a volume of 60 ml, which was, then, heat-sealed with an aluminum-containing closure member and was preserved under a condition of 23°C or 50°C. After preserved for a predetermined period of time, concentration of oxygen was measured by using a gas chromatography (GC-8AIT, GC-3BT, both manufactured by Shimadzu Seisakusho Co., detector: TCD (100°C), column: molecular sieve 5A(60°C), carrier gas: argon). The absorbed amount per a gram of the oxygen-absorbing composition was calculated from the concentration of oxygen, and was regarded to be the absorbed amount of oxygen.

(4) Observation of dispersion of unsaturated double-bonded polymer in the thermoplastic resin

[0133] A sample piece including an oxygen-absorbing layer and measuring 3 mm wide and 12 mm long was cut out from a panel portion of the multi-layer bottle or from the multi-layer film, and was buried and solidified in an epoxy resin by using a silicon mold. The sectional surface of the oxygen-absorbing layer was exposed by using the microtome, and the exposed surface only was washed with chloroform (special grade for high-speed liquid chromatograph: produced by Kishida Kagaku Co.) with stirring for one hour, dried for 12 hours, and was pre-treated by being deposited with Pt in vacuum with 10 mA for one minute. The sectional surface of the pre-treated bottle was observed by using a scanning electron microscope (JSM-6300F: manufactured by Nihon Denshi Co.) with an acceleration voltage of 10 kV.

(5) Measurement of the amino end group concentration (AEG)

[0134] 0.6 Milligrams of the sample was dissolved in 50 ml of a phenol/ethanol mixed solution (volume ratio of 4/1), and was titrated with stirring while adding 20 ml of an ethanol/water mixed solvent (volume ratio of 3/2). A 1/200 N ethanol hydrochloride/water mixed normal solution (volume ratio of 1/9) was used as a titration solution, and a methyl orange was used as an indicator. Further, the same operation was carried out without adding sample to conduct blank measurement.

[0135] The amino end group concentration (AEG) was found from the amount of titration in compliance with the following formula. When a transition metal catalyst was contained in the sample, AEG' was found by titration by dissolving the catalyst of the same amount only and was subtracted to find the AEG of the sample.

$$\text{AEG (eq/10}^6 \text{ g)} = \{[(V - V_0) \times N \times f/W] \times 10^3 - \text{AEG}'\}$$

V: amount (ml) of the 1/200 N ethanol hydrochloride/water mixed normal solution (volume ratio of 1/9) used for titrating the sample,

V₀: amount (ml) of the 1/200 N ethanol hydrochloride/water mixed normal solution (volume ratio of 1/9) used for the blank titration,

N: normality of ethanol/water mixed normal solution,

(Example 1)

[0146] A polymetaxylyleneadipamide (MXD6) resin (T-600: produced by Toyoboseki Co.) having a solubility parameter (Sp-value) of 11.6 and a amino end group concentration of 87 eq/10⁶ g as a thermoplastic resin and a cobalt neodecanoate (DICANATE5000: produced by Dainihon Ink Kagaku Kogyo Co.) having a cobalt content of 14% as a transition metal catalyst, were mixed together by using a tumbler so that the cobalt neodecanoate deposited on the surfaces of the MXD6 in an amount of 400 ppm calculated as cobalt. Then, the MXD6 resin on which cobalt has been deposited was extruded through a twin-screw extruder having a screw 37 mm in diameter while adding dropwise thereto a maleic acid-modified polybutadiene (M-2000-20, produced by Nihon Sekiyu Kagaku Co.) as an organic oxidizing component by using a liquid feeder, thereby to obtain an oxygen-absorbing resin composition containing the cobalt neodecanoate in an amount of 400 ppm calculated as cobalt and the maleic acid-modified polybutadiene in an amount of 5% by weight. The resin composition was fed into a T-die extruder to form an oxygen-absorbing film having a thickness of 20 μ m at a molding temperature of 260°C. The above film was laminated by using a multi-coater to obtain a multi-layer film of a constitution of 12- μ m PET/20- μ m oxygen-absorbing film/50- μ m PP. A cup sealed with the above multi-layer film as a closure member was boiled at 95°C for 30 minutes and was preserved at 30°C and 80%RH for 30 days to measure the amount of oxygen that has permeated into the container. The oxygen-absorbing film was confirmed for its easiness of formation, measured for its minimum length of dispersant and the amount of oxygen permeation. The results were as shown in Table 1.

(Comparative Example 1)

[0147] An oxygen-absorbing film was prepared under the same conditions as those of Example 1 but using a polybutadiene (B-2000, produced by Nihon Sekiyu Kagaku Co.) as an organic oxidizing component. However, gel was formed so much that a film could not be obtained, and no measurement was taken.

(Comparative Example 2)

[0148] An oxygen-absorbing film and a multi-layer film were prepared in the same manner as in Example 1 but using a polypropylene (PP)(Novak PPFG3D, produced by Nihon Polychem Co.) having a solubility parameter of 7.9 as a thermoplastic resin and effecting the molding at a temperature of 230°C, and were confirmed and measured in the same manner. The results were as shown in Table 1.

(Comparative Example 3)

[0149] An oxygen-absorbing film and a multi-layer film were prepared in the same manner as in Example 1 but using a polyethylene (PE)(Sumikasen L705, produced by Sumitomo Kagaku Co.) having a solubility parameter of 8.0 as a thermoplastic resin and effecting the molding at a temperature of 180°C, and were confirmed and measured in the same manner as in Example 1. The results were as shown in Table 1.

Table 1

	Film formation note 1)	O ₂ permeation (cc/cup) note 3)	Minimum length of dispersant (nm)
Example 1	○	0.0004	≤400
Comp.Ex.1	×(gelled)	—	note 2)
Comp.Ex.2	○	5.0991	≤400
Comp.Ex.3	○	4.8875	≤400

note 1) ○: favorably formed, good appearance

×: poorly formed, poor appearance

note 2) gels of the order of microns were formed much.

note 3) measured in compliance with (1)① above.

(Example 2)

[0150] A polyethylene terephthalate (PET)(J-125T, produced by Mitsui Kagaku Co.) was fed into an injector for forming inner and outer layers, and the resin composition prepared in Example 1 containing the MXD6, the cobalt neodecanoate and the maleic acid-modified polybutadiene, was fed into an injector for forming an intermediate layer, to co-injection mold them in an injection metal mold under the conditions of an injection nozzle temperature of 280°C and a resin pressure of 250 kgf/cm² to obtain a two-material-three-layer preform having the inner and outer layers of PET, the

(Example 6)

[0156] By opening a humidity-proof package and by using a T-die extruder (produced by Toshiba Kikai Co.) maintaining the T-die temperature at 270°C, a film having a thickness of 20 µm was formed from a resin composition of a polymetaxylyleneadipamide resin (T-600, AEG = 87 eq/10⁶ g, produced by Toyo Boseki Co.) dried under a pressure of not higher than 1 mmHg and a temperature of 150°C for 4 hours containing 5% by weight of a maleic acid-modified polybutadiene (M-2000-20 produce by Nihon Sekiyu Kagaku Co.) as an organic oxidizing component and 400 ppm of a cobalt neodecanoate (DICNATE 5000 produced by Dainihon Ink Kagaku Kogyo Co.) as a transition metal catalyst. A multi-layer film was formed by dry-laminating a biaxially stretched polyester film having a thickness of 12 µm on one surface of the film and an unstretched polypropylene film having a thickness of 50 µm on the other surface thereof by using a laminator. The multi-layer film was heat-sealed onto the opening of the above-mentioned HIRETOFLEX container and was preserved under the conditions of 30°C and 80%RH for 30 days to measure the amount of oxygen permeated into the container.

(Example 7)

[0157] A film was formed under the same conditions as those of Example 6 but using 5% by weight of a hydroxyl group-terminated polyisoprene (Poly ip produced by Idemitsu Sekiyu Kagaku Co.) as an organic oxidizing component and 310 ppm of the above-mentioned cobalt neodecanoate as a transition metal catalyst calculated as cobalt, to measure the amount of oxygen permeated into the container.

(Example 8)

[0158] A film was formed under the same conditions as those of Example 6 but setting the AEG concentration of the polymetaxylyleneadipamide resin to be 52 eq/10⁶ g, to measure the amount of oxygen permeated into the container.

(Example 9)

[0159] A film was formed under the same conditions as those of Example 6 but using the above-mentioned cobalt neodecanoate as a transition metal catalyst in an amount of 350 ppm calculated as cobalt, to measure the amount of oxygen permeated into the container.

(Example 10)

[0160] A film was formed under the same conditions as those of Example 6 but using the hydroxyl group-terminated polyisoprene as an organic oxidizing component in an amount of 3% by weight, to measure the amount of oxygen permeated into the container.

(Example 11)

[0161] A film was formed under the same conditions as those of Example 6 but using the maleic acid-modified polybutadiene as an organic oxidizing component in an amount of 8% by weight, to measure the amount of oxygen permeated into the container.

(Comparative Example 6)

[0162] A film was formed under the same conditions as those of Example 6 but setting the AEG concentration of the polymetaxylyleneadipamide resin to be 27 eq/10⁶ g, to measure the amount of oxygen permeated into the container.

(Comparative Example 7)

[0163] A film was formed under the same conditions as those of Example 6 but using the cobalt neodecanoate as a transition metal catalyst in an amount of 80 ppm calculated as cobalt, to measure the amount of oxygen permeated into the container.

(Comparative Example 8)

[0164] A film was formed under the same conditions as those of Example 6 but using the maleic acid-modified

[0169] The results of measurement were as shown in Table 4.

Table 4

	Amount of O ₂ permeation (cc/container) note 8)		Moldability
	No treatment	Boiled	
Ex. 12	0	-	good
Ex. 13	-	0	good
Ex. 14	0	-	good
note 8) Measured in compliance with (1)-(2) above.			

(Example 15)

[0170] An oxygen-absorbing layer was formed by using melt-kneaded pellets of a poly(m-xylyleneadipamide)(T-600, produced by Toyobo Co.) pelletized by using a twin-screw extruder, 5 wt% of a maleic acid-modified polybutadiene (M-2000-20, produced by Nihon Sekiyu Co.) and 310 ppm (calculated as cobalt) of a cobalt neodecanoate (DICNATE 5000, produced by Dainihon Ink Kagaku Kogyo Co.). A two-material-five-layer preform was obtained having a layer constitution of PET/oxygen-absorbing layer/PET/oxygen-absorbing layer/PET, and was biaxially stretched and blown under same conditions as those in Example 13, at stretching ratios of 2.4 times as great in the longitudinal direction, 2.9 times as great in the transverse direction and 6.96 times as wide in area, to obtain a two-material-five-layer bottle.

(Example 16)

[0171] A two-material-five-layer bottle was molded under the same conditions as those of Example 15 but maintaining the metal mold temperature at 180°C and effecting the heat-setting for 2.5 seconds, and was evaluated in the same manner as in Example 15.

(Example 17)

[0172] The preform same as that of Example 15 was heated at 100°C, and was biaxially stretched and blow-molded at stretching ratios of 3.3 times as great in the longitudinal direction, 3.5 times as great in the transverse direction and 11.55 times as wide in area by using a primary blow metal mold, in order to obtain a primary blow-molded article of a size larger than a final blow-molded article.

[0173] Next, the bottom portion, barrel portion and shoulder portion of the primary blow-molded article were shrunk by being heated in an oven heated at 800°C for 5 seconds.

[0174] In this case, the surface temperature of the molded article was 150°C in average.

[0175] Finally, the primary blow-molded article was biaxially stretched and blow-molded by using a secondary metal mold maintained at 180°C, and was heat-set for 2.5 seconds to obtain a two-material-five-layer bottle to evaluate it.

[0176] The multi-layer bottles of Examples 15 to 17 were evaluated to have permitted the permeation of oxygen in small amounts, and to have been shrunk little. The bottles had not been deformed as the parting after the biaxial stretching and blow-molding is excellent.

(Comparative Example 9)

[0177] A two-material-five-layer bottle was molded under the same conditions as those of Example 15 but without effecting the heat-setting in conducting the biaxial stretching and blow-molding in Example 15, and was evaluated.

[0178] As a result, it was learned that the amount of oxygen permeation and the shrinking of the container were larger than those of the multi-layer bottles of the above-mentioned Examples.

(Comparative Example 10)

[0179] A two-material-five-layer bottle was molded under the same conditions as those of Example 15 but effecting the heat-setting at a temperature of 130°C for 2.5 seconds in conducting the biaxial stretch blow-molding in Example 15, and was evaluated.

[0180] As a result, like in the above Comparative Example 9, it was learned that the amount of oxygen permeation

Table 5

Molding method	Stretch ratio (those of primary blow in the case of 2-step blow)			Heat-setting of shaping mold		Crystallinity (%)		Load at yield Point ($\times 10^7$ Pa)	
	Longi- tude	Trans- verse	Area	Temp. (°C)	Time (sec)	Inner layer	Outer layer	Inner layer	Outer layer
Example 15 1-step blow	2.4	2.9	6.96	150	2.5	30	32	9.8	10.6
Example 16 1-step blow	2.4	2.9	6.96	180	2.5	35	37	10.2	10.5
Example 17 2-step blow	3.3	3.5	11.55	180	2.5	53	54	11.6	11.9
Comp.Ex. 9 1-Step blow	2.4	2.9	6.96	none		26	17	8.1	8.0
Comp.Ex. 10 1-step blow	2.4	2.9	6.96	130	2.5	27	30	8.5	9.8
Comp.Ex. 11 1-step blow	2.4	2.9	6.96	180	6.0	56	57	—	—
Comp.Ex. 12 2-step blow	3.3	3.5	11.55	180	6.0	59	59	—	—

11.55 times as wide in area by using a primary blow metal mold, in order to obtain a primary blow-molded article of a size larger than a final blow-molded article.

[0191] Next, the bottom portion, barrel portion and shoulder portion of the primary blow-molded article were shrunk by being heated in an oven heated at 800°C for 5 seconds.

[0192] In this case, the surface temperature of the molded article was 150°C in average.

[0193] Finally, the primary blow-molded article was biaxially stretched and blow-molded by using a secondary metal mold maintained at 180°C, and was heat-set for 2.5 seconds to obtain a two-material-five-layer bottle to evaluate it.

(Example 21) (Pressure-resistant container)

[0194] A two-material-five-layer bottle was molded in the same manner as in Example 18 but without effecting the heat-setting in conducting the biaxial stretch blow-molding by using the secondary metal mold, and was evaluated.

(Comparative Example 13) (Pressure-resistant container)

[0195] A multi-layer bottle was molded in the same manner as in Example 18 but effecting the biaxial stretch blow-molding at stretching ratios of 1.8 times as great in the longitudinal direction, 2.2 times as great in the transverse direction and 3.96 times as wide in area.

[0196] As a result, the amount of oxygen permeation was large, and a portion under the neck of the multi-layer bottle became thick due to poor stretching.

(Comparative Example 14) (Heat-resistant container)

[0197] A multi-layer bottle was molded in the same manner as in Example 19 but effecting the biaxial stretch blow-molding at stretching ratios of 1.8 times as great in the longitudinal direction, 2.2 times as great in the transverse direction and 3.96 times as wide in area.

[0198] As a result, heat crystallization took place due to the heat-setting, and a thick portion under the neck of the multi-layer bottle became whitened due to the heat though the amount of oxygen permeation has decreased.

[0199] Table 6 shows the measured results of half-value widths of peaks of diffraction profiles of the above Examples and Comparative Examples based on the X-ray analysis, as well as the results of evaluation.

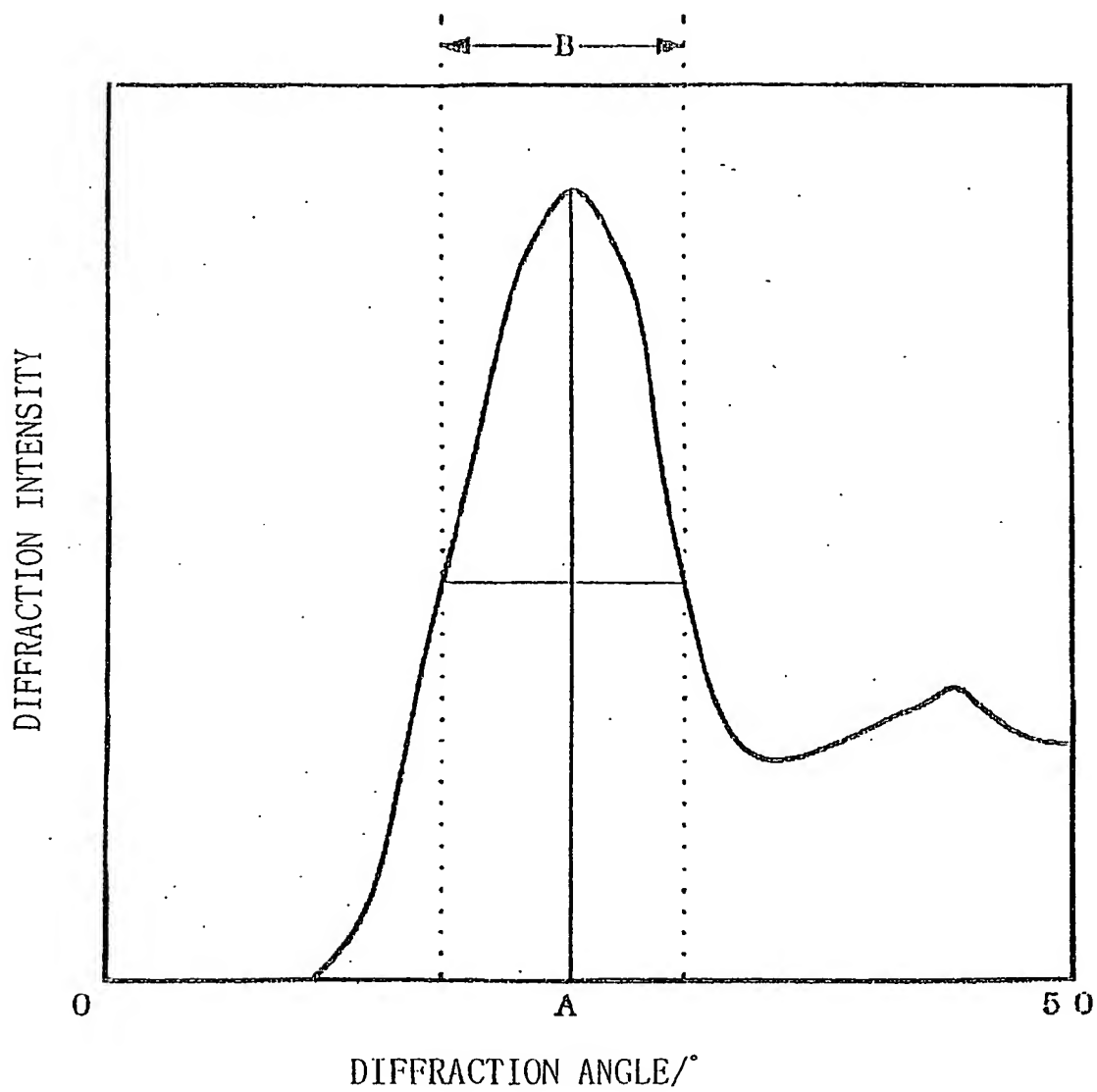
Table 6(continued)

Evaluation		
	O ₂ permeation (cc/month·bottle)	Bottle moldability/ appearance
Example 18	0.42	good
Example 19	0.18	good
Example 20	0.08	good
Example 21	0.10	good
Comp.Ex. 13	0.66	portion under neck becomes thick due to low stretch
Comp.Ex. 14	0.17	thick portion under neck is whitened

Claims

1. A resin composition obtained by blending a thermoplastic resin that can be melt-extruded at a solubility parameter of not smaller than 9.5 with an organic oxidizing component and with a transition metal catalyst, said organic oxidizing component being a polyene having a functional group on a side chain or at a terminal thereof.
2. A resin composition according to claim 1, wherein said the thermoplastic resin is a gas-barrier resin having an oxygen permeation coefficient of not larger than 7 cc·mm/m²·day·atm (20°C, 0%RH).
3. A resin composition accoring to claim 1, wherein said thermoplastic resin is a polyamide resin or an ethylene-vinyl alcohol copolymer.

Fig. 1





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EUROPEAN SEARCH REPORT

Application Number
EP 02 25 2505

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 367 835 A (TOYO SEIKAN KAISHA LTD) 16 May 1990 (1990-05-16) * examples *	1-12	
X	EP 0 301 719 A (MB GROUP PLC) 1 February 1989 (1989-02-01) * examples *	1-12	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 2 August 2002	Examiner Kolitz, R
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

02-08-2002

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5346644	A		JP 3183704 B2	09-07-2001
			JP 5115776 A	14-05-1993
			MX 9201379 A1	01-10-1992
			NO 921268 A	05-10-1992
			NZ 241802 A	22-12-1994
			PL 171849 B1	30-06-1997
			PL 172483 B1	30-09-1997
			RU 2092513 C1	10-10-1997
			US 5529833 A	25-06-1996
			US 5350622 A	27-09-1994
			ZA 9201914 A	16-09-1993
US 5310497	A	10-05-1994	AT 162689 T	15-02-1998
			AU 677240 B2	17-04-1997
			AU 5140293 A	26-04-1994
			BR 9307155 A	30-03-1999
			CA 2146026 A1	14-04-1994
			DE 69316765 D1	05-03-1998
			DE 69316765 T2	10-06-1998
			DK 663800 T3	30-03-1998
			EP 0663800 A1	26-07-1995
			ES 2113554 T3	01-05-1998
			FI 951537 A	23-05-1995
			IL 107137 A	13-07-1997
			JP 3218040 B2	15-10-2001
			JP 8502202 T	12-03-1996
			MX 9306020 A1	29-07-1994
			NZ 256613 A	20-12-1996
			WO 9407379 A1	14-04-1994
			US 5648020 A	15-07-1997
			ZA 9307137 A	27-03-1995
WO 9806779	A	19-02-1998	US 5776361 A	07-07-1998
			AT 213752 T	15-03-2002
			AU 724159 B2	14-09-2000
			AU 3963597 A	06-03-1998
			DE 69710734 D1	04-04-2002
			DK 918818 T3	25-03-2002
			EP 0918818 A1	02-06-1999
			JP 2001507045 T	29-05-2001
			NO 990674 A	19-03-1999
			NZ 333921 A	26-05-2000
			WO 9806779 A1	19-02-1998
US 5641825	A	24-06-1997	EP 0519616 A1	23-12-1992
			FI 922379 A	20-12-1992

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 25 2505

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

02-08-2002

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0301719 A	ZA	8804895 A	26-04-1989
	AU	618341 B2	19-12-1991
	AU	3344889 A	05-10-1989
	BR	8906385 A	28-08-1990
	CA	1324329 A1	16-11-1993
	DK	565389 A	10-11-1989
	EP	0335520 A1	04-10-1989
	WO	8908557 A1	21-09-1989
	GB	2216462 A , B	11-10-1989
	JP	2785405 B2	13-08-1998
	JP	3503153 T	18-07-1991
	KR	9608290 B1	24-06-1996
	US	5049624 A	17-09-1991
	ZA	8901864 A	28-02-1990